

# PATENT SPECIFICATION

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## (54) METHOD OF INTRODUCING PHOTOGRAPHIC ADDITIVES INTO SILVER SALT EMULSIONS

(71) We, AGFA-GEVAERT AKTIENGESELLSCHAFT, a body corporate organised under the Laws of Germany of 509 Leverkusen, Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of introducing a photographic additive which is a coupler, sensitising dye, stabilizer, white toner, UV absorber or UV stabilizer and which is substantially insoluble in water into photographic layers such as hydrophilic colloid binder layers or silver salt emulsions such as light-sensitive photographic silver halide emulsions or light-insensitive silver salt emulsions comprising silver salts of long chain carboxylic acids. The additives can be of any kind of colour-forming couplers, white couplers, coloured couplers, DIR couplers, diffusible dye releasing couplers, sensitizing dyes, white toners, UV absorbers and UV stabilizers. The additives are preferably of the kind which are capable of influencing the silver salt emulsions, e.g. sensitizing dyes or stabilizers.

The invention thus relates to a method of stabilizing or spectrally sensitizing silver salt emulsions by means of stabilizers or spectrally sensitizing dyes which are practically insoluble in water.

It is known that photographic additives, such as coupler compound or substances which are capable of being adsorbed on the grain surfaces of silver salts, such as sensitizing dyes or stabilizers, may be added to photographic silver halide emulsions in the form of solutions in suitable solvents such as methyl alcohol or dimethylformamide (see P. Glafkides, Photographic Chemistry, London, 1958, Volume II, pages 902 and 904).

These known methods, however, are unsuitable for the incorporation of couplers, stabilizers or spectrally sensitizing dyes which are practically insoluble in water and difficult to dissolve in the usual solvents because, as is known, excessive quantities of solvents cause difficulties connected with the diffusion or migration of the sensitizing dyes within the emulsion as described in Column 1 of German Patent Specification No. 1,964,169.

It is known that other emulsion additives such as colour couplers which need not be held on the surface of the silver halide crystal by adsorption after their introduction into the photographic emulsion can be incorporated in the silver halide emulsion in the form of dispersions. For this purpose, the coupler compound is usually dissolved in a suitable solvent which is generally immiscible with water, optionally in the presence of an oil former and suitable wetting agent, and then emulsified in an aqueous gelatine solution. The low boiling solvent is generally subsequently removed from the emulsion and the resulting dispersion is added to the photographic silver halide emulsion.

The application of such a method of incorporation for the purpose of

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spectrally sensitizing a silver halide emulsion has been described in German Patent Specification No. 1,547,705. In German Patent Specification No. 1,964,169 a process is described in which the preparation of a dispersion of spectrally sensitizing dyes in an aqueous gelatine solution is achieved by the following operations:

1. The sensitizing dye and an organic liquid which is miscible with water are ground up together and
2. the resulting ground material is added to an aqueous gelatine solution. In this process, the organic liquid has the object of producing a separating effect of the dye molecules during the grinding process and thus preventing agglomeration of the dyestuff particles.

A disadvantage of this known process, however, is that removal of the solvent from the resulting dispersion can only be achieved if low boiling organic solvents have been used, and even then only to a certain extent whereas attempts to remove polar solvents cause considerable problems. Polar solvents, in particular polar protic solvents, can be removed from gelatine dispersions only by heating, a process which has a very harmful effect on the stability of the sensitizing dye molecule. Moreover, removal of the solvent from the dispersion under vacuum may cause considerable foaming.

Even when non-polar solvents are used, all the known methods of removing low boiling solvents from aqueous dispersions are unsatisfactory in practice. If elevated temperatures are not used for evaporating off the solvent, only an insufficient quantity of solvent can be removed. Application of a vacuum is contraindicated by the foaming which is liable to occur, as already mentioned above, which is increased under vacuum conditions. Application of elevated evaporation temperatures, however, is unadvisable, as already mentioned above, owing to the readiness of the sensitizing dyes to decompose.

Residues of solvent left in the dispersion are a disadvantage for several reasons. First, even minute residues of solvent promote recrystallisation processes in the photographic layer, which deleteriously affect not only the additives which have been specially introduced but also other additives such as coupler compounds. Moreover, if residues of polar organic solvents which are miscible with water are left in silver halide emulsions, in particular in emulsions which are rich in silver and have a high silver packing density, they considerably reduce the stability of the casting emulsion, and this is shown in a reduced stability to digestion. The following problems are then liable to occur: Phase separation between the hydrophilic and hydrophobic phase, agglomeration and coalescence as well as flocculation before casting.

For a long time now there has therefore been a need for a process by which even photographic additives which are virtually insoluble in water, such as couplers, UV-absorbers, sensitizing dyes or stabilizers, can be incorporated in hydrophilic binder layers or in silver salt emulsion layers without any harmful effects to the emulsions or dispersions due to the presence of water-miscible or water-immiscible organic solvents and without the dispersions required for preparation of the emulsion layers undergoing any deleterious changes even when left to stand for prolonged periods.

It is an object of the present invention to provide a process by means of which even photographic additives which are practically insoluble in water, such as couplers, UV-absorbers, UV stabilizers, white toners, and preferably stabilizers and sensitizing dyes, can be incorporated in silver salt emulsions so that these emulsions can be effectively stabilized even with stabilizers which are insoluble in water and can be effectively sensitized with sensitizing dyes which are insoluble in water.

The present invention thus relates to a process for the introduction into a binder dispersion or into a silver salt emulsion of photographic additives which are substantially insoluble in water, which additives have been milled to a particle size of less than 1 micron and are preferably capable of influencing the sensitometric properties of the silver salt in silver salt emulsions, as is the case with stabilizers or sensitizers.

The process is characterised in that the substantially water-insoluble photographic additive which is a coupler, sensitising dye stabilizer, white toner, UV absorber or UV stabilizer is milled in the aqueous phase which is substantially free from organic solvents in the presence of a dispersing agent, which gives rise to a surface tension of not less than 38 dyn/cm in water when used in a quantity of 1 g/l, and the resulting aqueous dispersion is added to the emulsion to be cast, such as a

light insensitive hydrophilic colloid or to the silver salt emulsion, either immediately or after storage or after purification and isolation.

According to a preferred embodiment of the process according to the present invention, before the aqueous dispersion is added into a hydrophilic colloid solution, such as a photographic emulsion, it is dried under very mild conditions and thereby converted into a form which is very stable and durable and can easily be stored. In this form the dispersion of the additive can be added to the hydrophilic binder casting solution at any time without any need for heating and without causing any problems due to dissolution processes.

In contrast to the known methods, the method according to the invention consists of grinding the photographic additive without substantial amounts of any water-miscible organic solvent so that when the photographic additives are introduced into emulsions by the method according to the invention, no time and labour consuming removal of solvents from the resulting dispersions is necessary and, moreover, the emulsion layers are in no way affected by unwanted residues of organic liquids.

In addition, the method according to the invention requires no precautions for absorption of solvent from the surrounding atmosphere when the silver salt emulsion is being cast or dried, so that the method according to the invention does not give rise to any environmental problems.

In the method according to the invention, milling the photographic additive is carried out in an aqueous phase, i.e. a phase consisting mainly of water, e.g. distilled water or tap water. The aqueous phase may also contain minor quantities of the usual additives which may occur, for example, in tap water. Such additives may include calcium salts in quantities of not more than about 0.5% or traces of heavy metals. If desired, the aqueous phase may also contain hydrophilic binders such as gelatine or inorganic or organic salts such as sodium chloride or water softeners.

According to the invention, however, the aqueous phase does not contain substantial amounts of any organic solvents which would be capable of partially dissolving the photographic additives. The aqueous phase in which the photographic additive is dispersed may be completely free from organic solvents. It is, however, considered to be within the ambit of this invention, if the aqueous phase contains a very small amount or traces of an organic solvent, provided however, that such solvent does not exceed an amount of 1% by weight, based on the amount of photographic additive to be dispersed. Such small amount of organic solvent in the aqueous phase may have its origin from an organic solvent in which the photographic additive has been crystallized and which has not completely been removed from the additive. Also a very small amount of organic solvent such as amyl alcohol may have been deliberately added as an antifoaming agent.

According to the invention, milling is carried out in the presence of a dispersing agent. The term "dispersing agent" for surface active substances is in practice applied to organic compounds which are soluble in water but practically insoluble in water immiscible organic solvents and which, in contrast to typical wetting agents, reduce the surface tension of water by a smaller extent than these wetting agents, that is to not less than 38 dyn/cm when used at a concentration of 1 g/l of water.

Methods of introducing coupler compounds into photographic emulsions are known in the art, according to which couplers are milled in the presence of wetting agents and suitable coupler solvents.

It was surprising to find that, when wetting agents were used instead of dispersing agents in the process according to the invention, the results obtained were practically useless because the milling operation gave rise to extremely difficult problems. It was practically impossible to prevent foaming and the substance being milled migrated from the milling elements due to flotation so that further reduction to the required size was impossible.

The quantity of dispersing agent required in the process according to the invention, based on the quantity of photographic additive required to be dispersed, may vary within wide limits and depends mainly on the nature of the dispersing agent used and the particular photographic additive. It has generally been found to be sufficient to add from 0.1 to 3 parts by weight of dispersing agent to 1 part by weight of photographic additive but it is also possible to add more than 3 parts of dispersing agent.

When the additives used are e.g. spectral sensitizers or stabilizers, the aqueous dispersions prepared according to the invention are found to have excellent

stability in storage, particularly if an aqueous solution of a water-soluble polymer, e.g. an aqueous gelatine solution, has been added to the aqueous phase after milling and removal of the milling elements. An aqueous gelatine dispersion prepared in this way can be stored for months at room temperature without showing any signs of decomposition of the dispersed dye molecules or dispersed stabilizer molecules and hence without reduction of the spectral sensitizing effect or stabilizing effect after addition to the emulsion. 5

If desired, however, an aqueous dispersion containing peptides may be stored by casting it on a substrate and drying. After the desired storage time, the dried dispersion may be redissolved and added to the photographic emulsion. 10

In another embodiment of the process according to the invention, the aqueous dispersion is worked up under particularly careful and mild conditions to be converted into a very stable and durable form before it is introduced into the photographic emulsion. In this form, it can easily be added to the photographic emulsion at any time without any complicated operations to dissolve it and/or application of heat. 15

According to a preferred embodiment of the invention, the aqueous dispersion is worked up by drying in one of the usual apparatus of the kind employed in the art for working up formed pigments or dyes, e.g. paddle driers, disc atomizers or, preferably, apparatus of the kind which are suitable for atomization drying or freeze drying. 20

Freeze drying or atomization drying effects very careful removal of the water used for dispersion without causing any agglomeration or caking of the dispersed particles. 25

The apparatus used for atomization drying may be equipped with a one-material nozzle, which normally produces a granulate, or a two-material nozzle, which produces a powder. Further details about atomization drying may be found in the handbook by Ullmann, Enzyklopädie der Technischen Chemie, 4th Edition, Vol. 2, pages 255 et seq.

The particulate photographic additive produced in this way can be kept practically indefinitely and is extremely stable and can be stored in a very small space, which was impossible for additives prepared by the known processes. 30

The particulate photographic additive may be added to the liquid photographic emulsion at any time after its preparation. 35

If desired, however, the additive may first be mixed with water or an aqueous binder solution to produce an aqueous dispersion and added to the liquid photographic emulsion in this form.

The method of addition is immaterial and depends mainly on the nature of the photographic emulsion and the desired effect. For preparing an emulsion which has a low gelatine content but high silver content, direct introduction of the particulate photographic additive or introduction of the additive in the form of a highly concentrated aqueous dispersion are both suitable. 40

Examples of suitable dispersing agents which may be used according to the invention include monomeric, oligomeric and polymeric alkyl-aryl sulphonates, preferably having at least 18 carbon atoms. 45

Examples of monomeric alkyl-aryl sulphonates include the alkali metal salts of triisopropylnaphthalene sulphonic acids and di-sec.-butylnaphthalene sulphonic acids.

Examples of oligomeric and polymeric alkyl-aryl sulphonates include condensation products of naphthalene or ditolylether with formaldehyde and sulphuric acid or lignin sulphonic acids. 50

Milling of the photographic additives to reduce them to particle size of less than 1 micron is carried out in suitable mills of the kind already known but their shearing forces must be sufficient to reduce the material to be necessary particle size within a suitable length of time. Suitable mills of this kind are available commercially under the general heading of colloid mills. 55

Colloid mills which are particularly suitable for the process according to the invention are the so-called sand mills.

The following are examples of types of mills available on the market:

1. Sand mill manufactured by P. Vollrath, Maschinenfabriken, Köln
2. Bead mill manufactured by Draiswerke GmbH, Mannheim
3. Dyno mill manufactured by W. A. Bachofen, Maschinenfabriken, Basle.
4. Masap mills manufactured by Masap AG Matzendorf Schweiz

Processes and suitable mills have also been described in US Patent Specifications No. 2,581,414 and 2,855,156. 65

An example of a sand mill suitable for use on a laboratory scale is shown in Figure 1.

5 The container B for the milling process may be made of glass or steel. Steel containers used for the process according to the invention are preferably made of hardened steel to prevent excessive abrasion which would cause considerable contamination of the dispersion and hence of the photographic emulsion and may have a deleterious effect on the photographic properties of the emulsion. 5

10 The mill container B is enclosed in a cooling jacket K of PVC or metal and may be cooled during the milling process by a cooling liquid F. Running water used as coolant is generally sufficient to effect practically complete removal of the heat produced by milling and to ensure that the temperature of the material being milled does not rise above 40°C. The dimensions of the container are: Wall thickness 4 mm, internal width 75 mm, height 230 mm. A stirrer shaft R having a diameter of 15 mm and carrying four Duramid or Durethan discs 5 mm in thickness and 60 mm in diameter extends into the container. The four discs are arranged at intervals of 20 mm. 10

15 The shaft is rotated at the rate of 10<sup>4</sup> revs/min. by a drive motor M. The motor may be arranged centrally or laterally to the drive shaft and may drive the shaft via a cone belt. 15

20 The container is filled to about one third of its height and from about 5 to 80 g of substance are milled in each cycle. This requires the addition of at least about 3 to 4 times this quantity of milling elements. 20

25 The average particle diameter of the milling elements used depends on the particle diameter of the substance before it is milled. Optimum results are obtained if the average particle diameter of the substance to be milled is less than or equal to two-thirds of the particle diameter of the milling elements. If the substance to be milled has a greater particle diameter, it is advisable first to size reduce it by one of the usual methods. 25

30 The quantity of water required for milling may vary from 20 ml to 200 ml depending on the substance to be milled and the dispersing agent, and the quantity of dispersing agent used may also vary within wide limits, as already mentioned above. 30

35 A milling cycle is generally as follows: 40 g of substance to be milled are mixed with 200 g of glass beads, e.g. reflex beads of Dragonwerk Georg Wild, Bayreuth, having a diameter of from 0.85 mm to 0.95 mm, depending on the particle size of the substance to be milled, and the substance is then milled together with 100 ml of water and 15 ml of a 40% dispersing agent, using the laboratory sand mill described in Figure 1 (3 hours at a rate of stirring of 7000 revs/min). The temperature inside the mill is kept below 40°C by adjusting the rate of flow of cooling water. The whole contents of the mill are then filtered into a glass filter pot through a glass frit (pore size 40 to 90 µm). 35

40 According to one particular embodiment, the glass filter pot contains 2.5 l of a 10% gelatine solution which has been heated to 40°C. A further 2.5 l of a 10% gelatine solution are subsequently added to the filtrate and the volume of the resulting dispersion is made up to 10 l with water. 40

45 The filtrate obtained in this way is again briefly heated to 40°C and then stored at 4°C to solidify. The dispersion, which solidifies in a gel form, may now be added to the photographic silver halide emulsion either immediately or after further storage. 45

50 Instead of using the glass beads described above as milling elements, it is also possible to use quartz sand or silicon carbide sand. 50

55 According to the preferred embodiment, the filtrate obtained as described above is immediately subjected either to freeze drying or to spray drying, as will be described in detail below. 55

60 The photographic additive used in the process according to the invention is dispersed in the aqueous phase in the presence of dispersing agents without being dissolved. Particularly suitable are those additives which are practically insoluble in aqueous solutions, e.g. additives which have a solubility in water of less than about 1% to 20°C. 60

Non-diffusing slightly soluble colour couplers for the production of a yellow, magenta or cyan partial colour image are examples of photographic additives which may be dispersed according to the process of the present invention. In this respect reference may be had to the publication of W. Pelz in "Mitteilungen aus den Forschungslaboratorien der Agfa, Leverkusen/München", Vol. III, page 111

(1961) and K. Venkataraman in "The Chemistry of Synthetic Dyes", Vol. IV, 341—387, Academic Press (1971).

The non-diffusing colour couplers may carry in the coupling position a releasable substituent such that formation of dye only two equivalents of silver halide are needed in contrast to the conventional 4-equivalent couplers. Such 2-equivalent couplers are described e.g. in US Patent Specifications Nos. 3,408,194, 3,419,391, 3,476,563, 3,265,506, 3,519,429 and 3,458,315 and German Offenlegungsschriften DT-OS 2,057,941, 2,329,587 and 2,363,675. If the releasable substituent contains a chromophoric group, such as in the conventional masking couplers, the colour forming couplers generally are coloured with a colour suitable for masking the undesired side densities of image dyes, such as is known from US Patent Specifications 2,584,349, 2,453,661, 2,455,170 and 2,455,169. The image dyes produced from the colour couplers are generally non-diffusing.

However the image dyes, if formed by development, may first be diffusing and may be transferred to an image receiving layer, before they are converted into a non-diffusing form, as this is known from various dye-diffusion transfer processes, such as described in US Patent Specifications Nos 3,227,550 and 3,628,952 and German Patent Specification No. 1,772,929. In this case, the light sensitive silver halide emulsions have associated with them colourless or coloured non-diffusing dye-giving compounds which, during development, release diffusing dyes in image distribution. Such dye-giving compounds may be incorporated either to the silver halide emulsion layer or to an associated non-light sensitive hydrophilic binder layer which may contain development nuclei or silver halide capable of being developed without exposure.

Other compounds which may be incorporated according to the process of the present invention, are compounds which, during the reaction with oxidation products of colour-forming developers release substances capable of inhibiting the development of silver halide. Such compounds are the so called DIR couplers as described in US Patent Specification 3,227,554 or DIR compounds such as described in US Patent Specification 3,632,345. The said DIR couplers or DIR compounds carry a releasable thioether group which during the colour forming development is split off to form a diffusing mercapto compound which inhibits development of silver halide. Such compounds are suited to influence in colour-photographic materials the graininess, sharpness and gradation and hence the colour reproduction. The known DIR couplers form a dye simultaneously with the released inhibitor. The known DIR compounds as described in US Patent Specification No. 3,632,345 and in German Offenlegungsschriften Nos. 2,359,295 and 2,405,442 produce mainly colourless substances.

Photographic additives which are capable of coupling are preferably milled to form particles of less than 0.5  $\mu$ .

For the incorporation of coupler dispersions according to the process of the present invention, the process may be modified by adding a wetting agent to the dispersion either before or after drying and/or by adding a suitable oil-former to the dried dispersion of coupler. By the addition of wetting agents and/or oil-formers the reactivity of the dispersed coupler compound may be advantageously influenced.

Suitable wetting agents are those which are conventionally used for emulsifying of coupler compounds, such as those which substantially reduce the surface tension of water, such as alkali salts of sulphonated esterified fatty acids.

Suitable oil-formers are those which are conventionally used for emulsifying or hydrophobic photographic additives, preferably water-insoluble coupler solvents having a high boiling point, such as tricresylphosphate or dialkylphthalate. Other useful oil-formers are described e.g. in US Patent Specification No. 1,916,513. Such oil-formers are added to the aqueous coupler dispersion, preferably in emulsified form.

Dyes suitable for carrying out the process of the invention have already been disclosed in numerous Patent Specifications, for example some have been described in German Patent Specification No. 1,964,169.

The following Table A shows a number of spectrally sensitizing dyes which have been used in the examples described hereinafter.

Dyestuff-No.

TABLE A

Formula

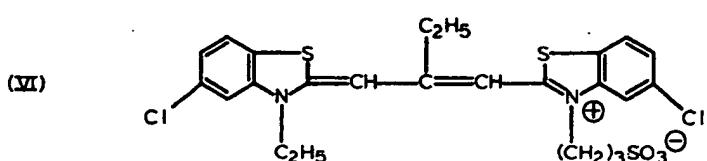
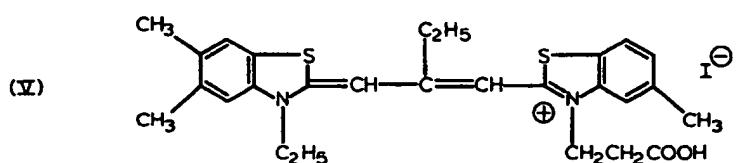
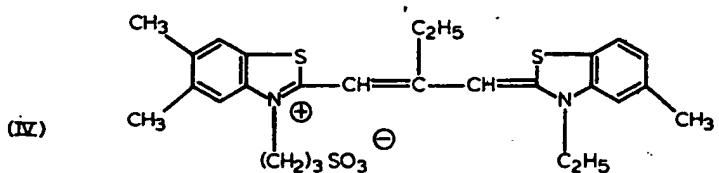
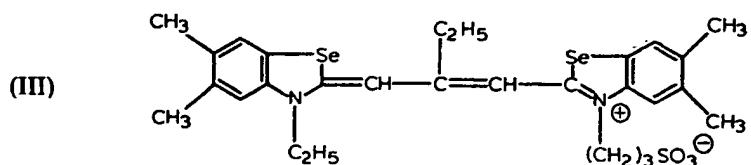
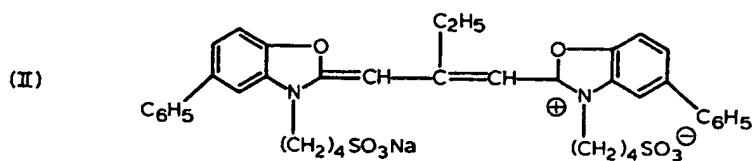
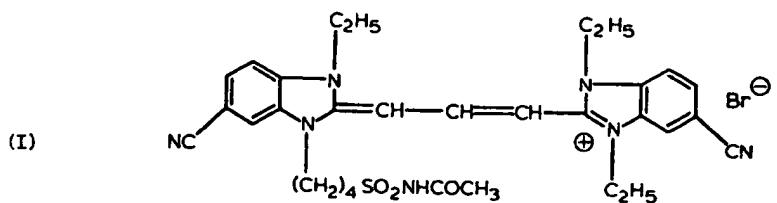
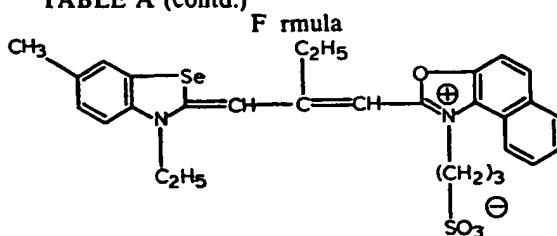


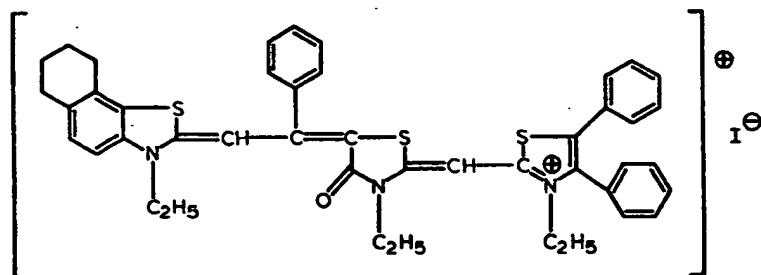
TABLE A (contd.)

Dyestuff-No.

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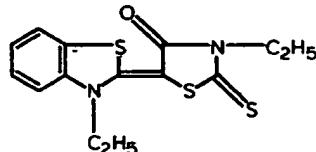


(VIII)



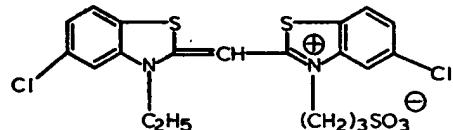
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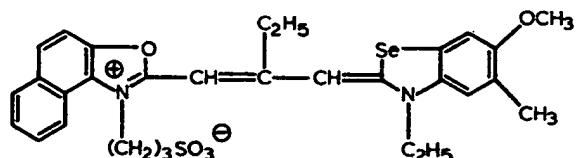


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The dye dispersions used in the process according to the invention may also contain binders, for example, gelatine. The proportion of dye to gelatine may vary within a wide range but, for spectral sensitization, the best results are obtained with dispersions in which the dye content is between 5 and 20%, based on the total weight of dye and binder. The dye dispersions used for spectral sensitization of photographic silver halide emulsions in the process according to the invention may also contain two or more dyes in each dispersion, or dispersions containing only one dye may be used in combination with two or more such dispersions. For achieving optimum sensitivity by the process according to the invention, the optimum concentration of dye incorporated in the emulsions may generally vary between about 0.2 to 4 g of dye per mol of silver halide in the emulsion, depending on the particular dye and emulsion used. Fine grained emulsions generally require a larger quantity of sensitizing dyes than coarse grained emulsions.

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Any photographic stabilizers may be used in the process according to the

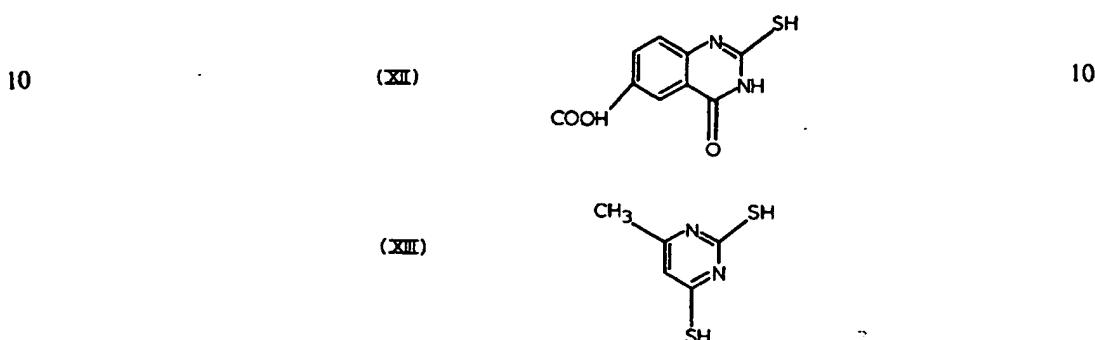
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inventi n. Particularly suitable again are those which are practically insoluble in aqueous solutions, e.g. stabilizers having a solubility of less than about 0.1% in water at 20°C.

5 Examples of such stabilizers are known and have been described in numerous publications, e.g. in US Patent Specification No. 3,692,527.

The following Table B shows stabilizers used in the examples described hereinafter.

TABLE B



The stabilizer dispersions used in the process according to the invention may also contain polymeric binders such as gelatine. The ratio of stabilizer to gelatine may vary over a wide range but, for stabilization, it has also generally been found suitable to use dispersions having a stabilizer content of from about 5 to 20%, based on the total weight of stabilizer and binder. For achieving sufficient stabilization by the process according to the invention, the concentration of stabilizer incorporated in the silver salt emulsions may be varied from 20 mg to 2 g of stabilizer per mol of silver salt, depending on the nature of the stabilizer and of the emulsion used.

According to the process of the present invention furthermore each desired photographic additive such as white couplers, white toners, UV-absorbers can be incorporated, and preferably those which are substantially insoluble in water.

The process according to the invention is, however, particularly suitable for the spectral sensitization or stabilization of any photographic silver salt emulsions. The light-sensitive silver halide may be dispersed in any hydrophilic colloids (binders) suitable for dispersing silver halides, e.g. gelatine; albumen; alginic acid; polyvinyl alcohol; polyvinyl pyrrolidone; cellulose ethers or partially hydrolysed cellulose acetate. The hydrophilic colloid may also contain dispersed vinyl polymers or water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulphoalkylacrylates or methacrylates.

Suitable photographic silver salt emulsions include light-sensitive silver halide emulsions or silver salt emulsions in which the silver salt consists partly or completely of light insensitive silver salts of long chain aliphatic carboxylic acids, in particular those having from 10 to 30 carbon atoms, e.g. silver salts of behenic acid or palmitic or stearic acid. Such silver salt emulsions may also contain silver halides which are added directly to the light insensitive silver salt emulsion or produced *in situ* on the grain surface of the light insensitive silver salts by addition of halides. Such emulsions include the so-called heat developable silver salt emulsions which are sensitive to light and to UV or IR radiation.

40 The silver halide emulsions used may be the usual silver chloride, silver bromide, silver chlorobromide or silver iodo-bromochloride emulsions.

The process according to the invention is particularly suitable for stabilizing or spectrally sensitizing photographic emulsions which have a high silver content.

45 By photographic emulsions having a high silver content are generally meant emulsions in which the proportion by weight of gelatine to silver expressed as silver nitrate is less than about 1. Emulsions of this kind have become known for use as film emulsions for photographic recording materials.

As a result of attempts to improve the sensitivity and sharpness of photographic recording materials, the silver halide packing density in modern

photographic emulsions is constantly being increased with a corresponding reduction in the proportion of binder. These emulsions frequently have a ratio of gelatine to silver of less than 0.7 to 0.2, in extreme cases as little as 0.1. For colour photographic purposes, emulsified colour couplers may be added to these emulsions. In such emulsions or casting melts, the resistance to digestion is extremely important and undesirably high quantities of residual solvent as well as substantial quantities of wetting agents which cause excessive reduction in the surface tension may make it impossible to obtain a uniform casting and hence to produce high quality materials. 5

The photographic additives such as colour couplers, white couplers, white toners and UV-absorbers, however, may also be incorporated into a non-light sensitive binder layer such as an intermediate layer. 10

The apparatus and procedure required for the drying processes such as spray drying or freeze drying used in the preferred embodiment of the invention are well known in the art and need not be described in detail here. Reference may be made, for example, to the handbook by Ullmann, Enzyklopädie der Technischen Chemie, 4th Edition, pages 712 et seq and 716 et seq and "Das Trocknen" in the series "Grundlagen der chemischen Technik" by Dr. Ing. Friedrich Kneule, 3rd Edition, 1975, in which methods of freeze drying are described on pages 472 et seq and of atomization drying on pages 401 et seq. 15

In the spray drying process, drying itself, may, if desired, be carried out in an inert gas atmosphere. For freeze drying, it is particularly advantageous first to carry out a process of shock freezing, e.g. using liquid nitrogen, followed by the usual sublimation at elevated temperatures which must, however, be below the melting point of the dispersion. 20

The process according to the invention is particularly advantageous for the introduction of photographic additives which contain water-solubilizing groups such as sulphy groups but which are not sufficiently water-soluble to allow them to be introduced as aqueous solutions into photographic emulsions. When such photographic additives are first emulsified in an aqueous gelatine solution by the process described in German Patent Specifications No. 1,547,705 and 1,964,169, the photographic additives are liable to be adsorbed so firmly on gelatine as a result of van der Waals interaction that, when the aqueous gelatine dispersion is subsequently introduced into the photographic silver salt emulsion, the capacity of the photographic additive to influence the sensitometric properties of the silver salt are progressively reduced. 25

If such additives are converted into a particulate form by one of the above mentioned drying methods in the process according to the invention, they can be stored indefinitely without suffering any loss of their capacity to influence silver salts in photographic emulsions. 30

The invention will now be described in more detail with reference to the following examples. 35

**EXAMPLE 1**

3 g of sensitizer VIII were stirred up with 7 g of the sodium salt of di-(sulphonaphthyl)-methane with the addition of a small quantity of water (about 50 ml) and the slurry obtained was then milled with 200 g of quartz sand having an average particle diameter of about 1 mm in a sand mill, e.g. as illustrated in Figure 1, for 2 hours. 40

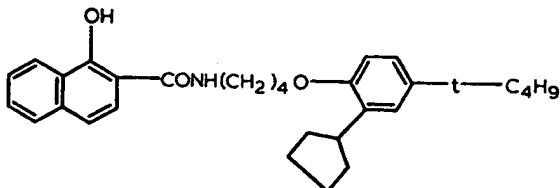
The sensitizer compound used had an average particle size before milling of about 0.6 mm. After milling, it had an average particle size of 0.5  $\mu\text{m}$  (if the sensitizer has a particle size of more than 0.6 mm before milling, it must first be reduced to a particle size of less than or equal to 0.6 mm in an ordinary mill before it is milled in a sand mill as described above). The proportion of the particle size of the substance which is required to be milled and the diameter of the milling elements should always be optimized. A useful rule of thumb is that the best results are always obtained when the average particle diameter of the substance to be milled is less than or equal to 2/3 of the average particle diameter of the milling elements. 45

The aqueous dispersion obtained as described above was shock frozen with liquid nitrogen after removal of the milling elements and then stored in the dry state after sublimation. 50

A sample containing 260 mg of sensitizer was added immediately, and other samples at intervals of 4 weeks, to 1000 g of a silver halide emulsion which had been prepared as described below. 55

60

5 To 1000 g of a silver iodobromide emulsion having a silver halide content of 0.55 mol per kg were added 100 ml of a 1% aqueous solution of 4 - hydroxy - 6 - methyl - 1,3,3a,7 - tetrazaindene, 20 ml of a 1% aqueous pyrocatechol solution and 50 ml of a 5% sodium salt solution of pentadecylene succinic acid diglycolide. 42 g of cyan colour coupler of the formula 5.



10 were added to the silver halide emulsion in the form of a coupler dispersion prepared by emulsifying the colour coupler together with 21 g of dibutylphthalate and 4.2 g of dodecyl benzene sulphonate sodium in 400 ml of a 2.5% gelatine solution. 10

The photographic emulsions obtained were sensitometrically assessed in the usual manner after they had been cast on a transparent cellulose triacetate substrate.

15 Sensitometric assessment showed that the individual photographic materials prepared from the individual samples were completely identical in their sensitivity, gradation and maximum density over a period of half a year. 15

The sensitizing effect of the sensitizer was not reduced by storage in the dry state.

20 A photographic material which had been prepared as described above except that the sensitizer dispersion was immediately added to the silver halide emulsion after milling in the sand mill was also sensitometrically assessed for comparison. 20

This assessment of the sensitometric results showed that the photographic emulsion which had been sensitized with freshly prepared sensitizer dispersion provided the same results with regard to sensitivity, gradation and maximum density as emulsions which had been sensitized with freeze dried sensitizer. 25

25 The comparison shows that the effect of the spectral sensitizer has in no way been deleteriously affected by the freeze drying treatment. 25

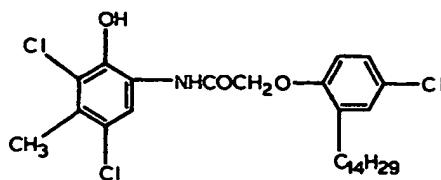
#### EXAMPLE 2

30 80 g of sensitizer or stabilizer were mixed with 250 g of glass beads obtainable under the name of reflex beads (Dragonwerke, Bayreuth) having a diameter of from 0.85 mm to 0.95 mm and the mixture, together with 100 ml of water and 3 ml of a 40% aqueous solution of a polymeric alkyl naphthalene sulphonate, was milled for 3 hours in a laboratory sand mill illustrated in Figure 1, which was operated at a speed of 7000 revs/min. The temperature inside the mill is kept below 40°C by adjusting the rate of supply of cooling water. The whole contents of the mill were then filtered through a glass frit having a pore diameter of from 40 to 90  $\mu$  into a glass filter pot containing 5 l of a 10% gelatine solution which had been heated to 40°C. When the filter had been thoroughly washed, a further 5 l of liquid 10% gelatine solution were added to the filtrate. The volume was then made up to 20 l with water. 30

35 The resulting filtrate was again briefly heated to 40°C and stored at 4°C to solidify. The dispersion, which solidified in the form of a gel, could be immediately added to the silver halide emulsion for sensitization or stabilization purposes or it may first be stored for any length of time. 40

40 Sensitizer dispersions prepared as described above contain, in the disperse form, one of the above mentioned sensitizers I to XI while the stabilizer dispersions contain one of the above mentioned stabilizers XII or XIII. The sensitizer or stabilizer dispersions are then added to the silver halide emulsions as described below. 45

50 1 kg of a silver iodobromide emulsion containing 1 mol of silver halide per kg was spectrally sensitized with one of the sensitizer dispersions described above, containing 260 mg of sensitizer IV, and a colour coupler dispersion obtained by emulsifying 30 g of the colour coupler described in Example 1, 12 g of colour coupler of the formula 50



21 g of dibutyl phthalate and 4.2 g of dodecylbenzene sulphonate sodium in 300 ml of an aqueous gelatine solution containing 10 g of gelatine, were then added. Emulsion A, which was now ready for casting, was transferred to a circulatory system tempered at 40°C and driven by a Centrichem rotary pump of ECO-Pump Corporation.

For comparison, a similar colour coupler containing silver halide emulsion B was prepared except that the sensitizer was added to the silver halide emulsion in the form of a 0.05% solution in dimethylformamide instead of by the method according to the invention.

Small portions were removed from both samples at intervals of 4 hours and examined microscopically.

Another small portion was applied to a transparent cellulose triacetate substrate and, after hardening with a water-soluble carbodiimide and the usual photographic processing (colour development with colour developer N - ethyl - N -  $\beta$  - oxyethyl - 3 - methyl -  $p$  - phenylenediamine at 38°C for 3½ minutes), it was examined to determine the gradation and surface gloss.

Both in the microscopic investigation and in the examination for surface gloss, the photographic emulsion containing colour coupler was examined to determine the resistance of the colour coupler to crystallisation. Crystallised colour coupler compounds can either be seen microscopically or detected by the resulting clouding or matting of the surface of the resulting photographic material.

The following results were obtained:

25	Sample	Digestion time (hours)	Gradation		Surface gloss	Crystallisation	25
			$\gamma_1$	$\gamma_2$			
30	A	0	0.68	1.04	glossy	no crystals	30
	B	0	0.65	1.05	glossy	no crystals	
	A	8	0.65	1.07	glossy	no crystals	
	B	8	0.58	0.98	slight matting	isolated crystal plates	
35	A	24	0.70	1.10	glossy	no crystals	35
	B	24	0.48	0.75	very severe matting due to crystallisation	mainly octagonal crystal plates	

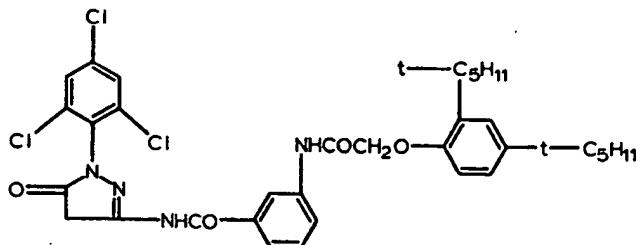
The experiment shows that the presence of dimethylformamide in the casting solution reduces very considerably the resistance to digestion so that crystallisation phenomena can be observed after a digestion time of only 8 hours. A comparison of the photographic materials shows that if the comparison casting solution has been digested for 8 hours, its use for photographic materials is difficult since the photographic properties, expressed by the gradation values  $\gamma_1$  and  $\gamma_2$  and by the surface gloss of the photographic material, are considerably impaired. The comparison also shows that photographic casting solutions prepared in accordance with the invention have excellent resistance to digestion and produce excellent photographic materials in which the properties are in no way deleteriously affected by prolonged storage of the casting solution.

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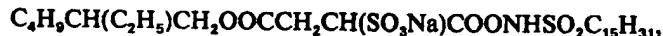
### EXAMPLE 3

A) 1 kg of a silver iodobromide emulsion containing 1 mol of silver halide was spectrally sensitized by means of a sensitizer dispersion which had been prepared as described in Example 2 and contained 130 mg of sensitizer I. To this sensitized emulsion were then added 150 ml of a 1% aqueous solution of 4 - hydroxy - 6 -

methyl - 1,3,3a,7 - tetraazaindene, 2 ml of a 50% aqueous glycerine solution and 35 g of magenta coupler of the formula



5 together with 35 g of tricresylphosphate and 3.5 g of sodium dodecylbenzene sulphonic emulsified in 250 ml of 3.5% aqueous gelatine solution. 60 ml of a 4% solution of a wetting agent of the formula



10 5 ml of a 1 N sodium hydroxide solution, 5 ml of a 5% solution of chromium acetate and 30 ml of a 1% pyrocatechol solution were then added.

10 B) The procedure is the same as that described for sample A) except that a sensitizer dispersion prepared as described in Example 2 and containing 130 mg of sensitizer II was also added.

15 C) The procedure is the same as that described for sample B) except that, in addition, a stabilizer dispersion prepared according to Example 2 and containing 65 mg of stabilizer compound XII was added.

20 For comparison, comparison compositions D) to F) were prepared by the method described for samples A) to C) except that instead of using sensitizer dispersions or stabilizer dispersion, sensitizer I was added to the silver iodobromide emulsion in the form of a 0.1% methanolic solution, sensitizer II was added in the form of a 0.05% methanolic solution and the stabilizer in the form of a 0.05% methanolic solution. In Figure 2, the resulting viscosity values  $\eta$  of the individual casting solutions of samples D) to F) are plotted against the quantity of methanol added. It can be seen that even a small addition of methanol to the casting solution causes severe changes in viscosity. In contrast to the comparison samples, samples A), B) and C) are virtually independent in their viscosity on the nature and quantity of sensitizer or stabilizer added, and their viscosities are 39.5, 39 and 38.5. cp. Moreover, the viscosity of emulsions prepared according to the invention is approximately the same as that of an emulsion which has been prepared in a similar manner but using pure gelatine solution instead of the sensitizer dispersion. In comparison solutions E) and F), the viscosity is already so much reduced that casting on a film substrate does not result in the formation of a photographic layer containing a sufficient quantity of silver halide. Due to sedimentation phenomena, low viscosity casting solutions become depleted of silver halide in the casting apparatus at the point where the film substrate dips into the solution so that, with low viscosity casting solutions, it is not possible to obtain layers containing more than a small quantity of silver halide.

#### EXAMPLE 4

40 100 ml of a 1% aqueous solution of 4 - hydroxy - 6 - methyl - 1,3,3a, 7 - tetraazaindene, 20 ml of a 1% aqueous pyrocatechol solution and 50 ml of a 5% solution of the sodium salt of pentadecylene succinic acid diglycolide were added to 1000 g of a silver iodobromide emulsion containing 0.55 mol of silver halide per kg. As colour coupler were used 42 g of the colour coupler described in Example 1 in emulsified form together with 21 g of dibutyl phthalate and 2.1 g of dodecylbenzenesulphonic acid sodium in 420 ml of 25% gelatine. The emulsion was sensitized by the method described in Example 3. Comparison sample H was sensitized with 190 mg of sensitizer dye III in the form of a 0.05% solution in a mixture of methanol and dimethylformamide (volumetric ratio 1:1) while sample G according to the invention was sensitized with a sensitizer dispersion according to Example 2 containing 190 mg of sensitizer III. The samples prepared in this way were stored at 40°C. This storage at 40°C is in practice a necessary part of preparation for casting. When the solutions ready for casting were stored at 40°C,

the comparison composition H showed signs of considerable sedimentation of the dispersed silver halide grains. By contrast, sample G according to the invention was seen to be much less susceptible to sedimentation.

5 The silver halide emulsion used in Example 4 was an emulsion containing silver halide grains in which the most frequently occurring grain diameter was about 0.55  $\mu\text{m}$ . The percentage proportion of silver halide grains containing the most frequent grain diameter was about 15%.

Curve 1 of Figure 3 represents the frequency of individual grains plotted against their grain diameter in percent.

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#### EXAMPLE 5

10 Example 4 was repeated except that the silver iodobromide emulsion used was replaced by an emulsion which was similar except that the silver halide grains having the most frequently occurring grain diameter of 0.6  $\mu\text{m}$  was present only to an extent of about 8% while a larger proportion of the silver halide grains than in the comparison emulsion of Example 4 had a grain diameter of 1  $\mu\text{m}$  and 2  $\mu\text{m}$  and the proportion of coarse grained silver halide grains was considerably higher than in Example 4. A comparison of the frequency distribution of two emulsions can be seen in Figure 3, in which curve 2 represents the frequency distribution of silver halide grains in the emulsion used in Example 5 while curve 1, as already mentioned above, represents the frequency distribution in the emulsion of Example 4.

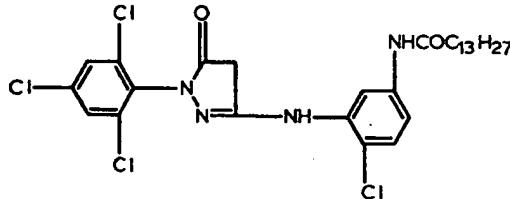
15 Figure 4 shows the results obtained from sedimentation measurements. Along the ordinate are plotted the height in the storage tank (filling height 40 cm) from which the individual samples for measurement were removed and along the abscissa are entered the silver content found at these different heights, measured as g of silver nitrate per kg of emulsion. The measurements represented in Figure 4 were carried out after the emulsion had been left to stand for 6 hours. Curves G and H represent the values obtained with emulsions of Example 4 and curves G' and H' the values obtained with emulsions of Example 5. Curves G and G' are obtained 20 from samples according to the invention and curves H and H' from comparison samples.

25 The comparison shows that photographic emulsions prepared according to the invention have much less tendency to sedimentation phenomena than comparison emulsions, the results depending on whether the silver halide emulsions used are 30 comparatively homodisperse or heterodisperse.

#### EXAMPLE 6

35 This example shows that compared with processes known in the art, the sensitization process according to the invention is capable of producing photographic materials with improved sensitivity.

40 To 1 kg of an iodobromide emulsion (silver content 0.3 mol per kg) containing 4 - hydroxy - 6 - methyl - 1,3,3a - 7 - tetraazaindene, a pyrocatechol solution and a sodium salt solution of pentadecylenesuccinic acid diglycolide were added 24 g of 45 coupler of the formula



45 in an emulsified form with 6 g of dibutyl phthalate and 180 g of a 2.5% aqueous gelatine solution.

50 Sensitization was carried out by the process described in Example 2. Sample I according to the invention was sensitized with a sensitizer dispersion according to Example 2 containing 45 mg of sensitizer I while comparison sample K was sensitized with 45 mg of sensitizer I dissolved to form a 1:1000 solution in methyl alcohol.

55 Each of the resulting emulsions was hardened with 2 ml of a 5% triacryloformal solution and cast on a transparent cellulose triacetate substrate.

5 After exposure and development of the photographic materials, using N - butyl - N -  $\delta$  - sulphobutyl - p - phenylene diamine as developer substance at room temperature, comparison shows that the sample according to the invention is more sensitive by 1.5 DIN than the comparison sample to which the sensitizing dye had been added in methanolic solution. 5

10 Other samples according to the invention L and N and comparison samples M and O were prepared in a similar manner except that, for comparison with sample I and with comparison sample K, instead of using 45 mg of sensitizer II, only 20 mg were used in samples L and M and 10 mg in samples N and O. 10

15 When the sensitometric results are assessed, it is surprisingly found that even when smaller quantities of sensitizer are used in the materials according to the invention, these materials still show a sensitivity gain of from 1 to 1.5 DIN compared with comparison samples K, M and O. 15

#### EXAMPLE 7

15 Another comparison example shows the advantage obtained with the process according to the invention when freeze dried sensitizer dispersions are used, in comparison with processes known in the art. 15

20 120 ml of a 1% aqueous solution of 4 - hydroxy - 6 - methyl - 1,3,3a,7 - tetraasaindene and 1 ml of glycerol were added to 1 kg of an iodobromide emulsion (0.7 mol of silver per kg). The colour coupler used consisted of 42 g of the colour coupler described in Example 6 added in emulsified form in 12 g of dibutyl phthalate in 180 g of a 2.5% gelatine solution. 20

25 The emulsion was sensitized with 110 mg of sensitizer II which had been pretreated as follows: 25

30 10 g of sensitizer II were milled as described in Example 1 with 23.3 g of a condensation product of naphthalene with formaldehyde and sulphuric acid (average molecular weight 420) as sodium salt, 100 g of sand and 100 ml of water. The sand was then filtered off and the filtrate shock frozen with liquid nitrogen while the water was removed by sublimation under vacuum at a temperature below the melting point of the crystallised aqueous phase. 1 g of the resulting product was taken up in 75 ml of water and from it, the quantity corresponding to 110 mg of sensitizer was added to the emulsion previously described. 30

35 Working up the emulsion, preparation of the photographic material, exposure and processing were carried out as described in Example 6. 35

40 A comparison material Q was prepared in a similar manner. In contrast to material P prepared according to the invention, it was sensitized with 110 mg of sensitizer which had been emulsified as described below before it was added to the emulsion: 40

45 1 g of sensitizer II was dissolved in a mixture of 50 ml of m-cresol and 25 ml of methyl alcohol and to this solution was added a solution of 3.33 g of a 50% aqueous sodium dodecylbezene sulphonate paste in 17 ml of ethyl acetate. 45

The combined solutions were then emulsified in 350 ml of a 6% gelatine solution with vigorous stirring and the volume of the emulsion was then made up to 100 ml with water. A quantity of this sensitizer emulsion which corresponded to 110 mg of sensitizer was added to 1 kg of the above described silver halide emulsion.

The comparison shows that the sensitivity of material P prepared according to the invention is higher by one DIN unit than that of the comparison material Q. 45

#### EXAMPLE 8

50 1 kg of a silver iodobromide emulsion containing 1 mol of silver halide per kg and provided in the form of a mixture of a conventional silver iodobromide emulsion with a convert emulsion in proportions of 8:2 was made ready for casting, using the cyan coupler and additives indicated in Example 2. 50

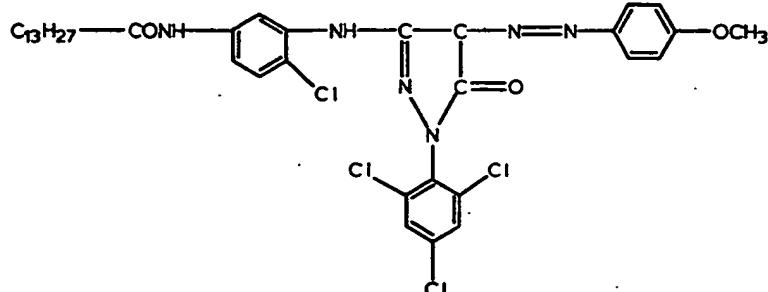
55 The emulsion was sensitized with 130 mg of sensitizer V and 130 mg of sensitizer III. In sample R according to the invention, the sensitizer mixture was dispersed in a dilute gelatine solution by the method described in Example 2 whereas in comparison sample S the sensitizer mixture was added as a 0.05% solution of sensitizer V in dimethylformamide and as a 0.1% solution of sensitizer III in methyl alcohol. 55

60 When the resulting emulsions had been cast and hardened with a water-soluble carbodiimide, the photographic materials obtained were exposed and then developed in the usual manner, using N - ethyl - N -  $\beta$  - oxyethyl - 3 - methyl - p - phenylene diamine as developer substance. Sensitometric assessment shows 60

that, in comparison with sample S of the known art, Sample R according to the invention has gained in sensitivity by two DIN and its colour fog is reduced by 0.06 colour density units.

#### EXAMPLE 9

5 20 g of the yellow masking coupler of formula



10 and 20 g of the sodium salt of the condensation product of 2 mols of ditolyl-ether, 1 mol formaldehyde and 2 mols  $H_2SO_4$  are milled together with a small amount of water in a sand mill such as shown in Figure 1 to form particles having an average particle size of less than  $0.5 \mu$ . The obtained dispersion is divided into two parts and one part is spray dried and the other part is directly used as described below.

15 Each part of the dispersion described above is added to 1 kg of a green sensitized silver bromide iodide emulsion having a silver content of 0.8 mols. To both emulsions are added 10 g of tricresyl phosphate, emulsified in 70 g of a 3.5 per cent by weight aqueous gelatine solution with the addition of sodium dodecyl benzene sulphonate.

20 The obtained casting solutions are cast on a transparent cellulose triacetate support to a silver coating of 3 g/m<sup>2</sup> and hardened with a water soluble carbodiimide to a swelling factor of 3.2. The sensitometric assessment shows that both samples show completely identical results with respect to sensitivity gradation and maximum colour density as well as graininess and surface gloss. It is evident from this that the quality of the masking coupler dispersion has not been impaired by the drying.

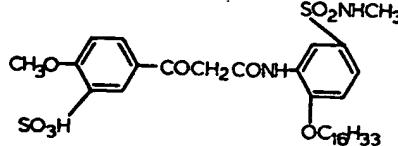
25 For comparison another photographic material was produced with the difference that the coupler instead of being used in form of a spray dried dispersion was incorporated into the silver halide emulsion as follows. 10 g of the masking coupler are heated together with 10 g of tricresyl phosphate and 20 ml of ethylene chloride. The solution was emulsified in 70 ml of a 3.5 per cent by weight gelatine solution, containing 1 g sodium dodecyl benzene sulfonate as wetting agent.

30 A sample of each the photographic material of the present invention as well as the comparison material was subsequently exposed in a sensitometer behind a grey continuous wedge and processed in a colour developer containing N - ethyl - N -  $\beta$  - oxyethyl - 3 - methyl - p - phenylenediamine at 38°C and fixed, bleached and rinsed. The assessment of sensitometric results shows that the fog in the comparison material is higher by 0.3 colour density units, as compared with the sample of the invention. This would require in a reversal process an additional reversal exposure. As regards the gradation and sensitivity both materials were identical.

#### EXAMPLE 10

40 The following example shows that coupler compounds which are soluble in alkali in contrast to their insoluble barium salts give rise to an undesired increase to viscosity of the casting emulsion. When, however, water insoluble salts are incorporated according to the process of the invention, the viscosity of casting solutions is not influenced disadvantageously.

45 38 g of a yellow forming coupler of the following formula



are added as a 5 per cent by weight aqueous solution having a pH of 6.5 to 1.0 kg of a silver chloride bromide emulsion. The emulsion contained a wetting mixture of saponine and a compound of the following formula



5 and was hardened with triacryl yl formal (2 per cent by weight, based on gelatine) and was cast on a polyethylene coated paper to a silver coating of 1.2 g of  $\text{AgNO}_3/\text{m}^2$ .

10 The photographic material obtained was exposed as usual and colour-developed at 25°C with N - butyl - N -  $\delta$  - sulphobutyl - p - phenylenediamine.

15 For comparison a photographic material was prepared according to the invention with the difference that instead of a free yellow forming coupler compound a 5 per cent aqueous dispersion of the corresponding barium salt was used, which has been prepared as described in Example 9 and after spray drying was incorporated in water. The dispersion contained as dispersing agent the condensation product of 2 mols of naphthalene, 1 mol of formaline and 2 mols  $\text{H}_2\text{SO}_4$  in an amount of one part per one part of barium salt.

20 The assessment of sensitometric results shows that the material according to the invention and the comparison material have the same results as regards sensitivity, gradation and maximum colour density. However, the viscosity of the casting solution used for comparison is substantially higher if measured after a standing time of one hour than the casting solution according to the present invention. The viscosity of the casting solution of the present invention was 8 cP and that of the comparison casting solution was 76 cP.

#### EXAMPLE 11

25 10 g of sensitizer XI together with 7 g of the sodium salt of the condensation product of formaline ditolyl ether and sulphuric acid and a small amount of water (about 50 ml) were mixed to form a slurry and subsequently milled in a sand mill such as shown in Figure 1 for two hours together with 200 g of quartz sand having an average grain diameter of about one mm. The used sensitizer compound which 30 prior to milling had an average grain size of about 0.5 mm had after milling an average grain size of less than 0.5  $\mu\text{m}$ . If the sensitizer has a particle size of more than 0.6 mm before milling it must first be reduced to a particle size of less than or equal to 0.6 mm in an ordinary mill before it is milled in a sand mill as described above. The portion of the particle size of a substance which is required to be milled and the diameter of the milling elements should always be optimized. A useful rule of thumb is that the best results are always contained when the average particle diameter of the substance to be milled is less than or equal to 2 thirds of the average particle diameter of the milling elements.

35 After separation from the milling elements the obtained aqueous dispersion was shock-frozen with liquid nitrogen and then stored in the dry state after sublimation.

40 A sample containing 180 mg of sensitizer was added immediately and other samples at intervals of 4 weeks to 1000 g of a silver halide emulsion which had been prepared as described in Example 1.

45 The sensitometric assessment showed that the individual photographic materials prepared from the individual samples were completely identical in their sensitivity gradation and maximum density over a period of half a year.

#### EXAMPLE 12

50 A light-sensitive element of a photographic material for the dye diffusion transfer process was prepared by casting on a transparent cellulose triacetate layer support, the following layers (the given amounts are those per 1  $\text{m}^2$ ).

1. An image receiving layer containing 3.8 g of octadecyl trimethyl ammonium-methyl sulphonate and 9.5 g of gelatine.
2. A reflecting layer containing 48.5 g of  $\text{TiO}_2$  and 4.85 g of gelatine.
3. A dye layer containing 1 g of a compound of the following formula

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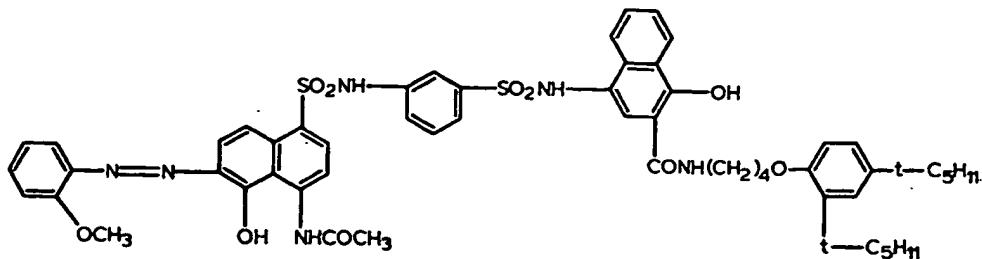
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0.1 g of carbon black and 2.56 g of gelatine.

4. A direct positive working unfogged green sensitized silver bromide iodide emulsion containing silver in an amount equivalent to 2.5 g of silver nitrate.

5. A protecting layer of gelatine.

The uppermost layer of the light sensitive element was covered with a transparent cover sheet containing a copolymerise of acrylic acid and acrylic acid ester.

10 A processing paste was distributed between the light sensitive element and the cover sheet. The processing paste had the following composition:

25 g of KOH

10 ml of benzyl alcohol

3 g of benzotriazole

0.25 g of ascorbic acid

15 1.0 g of acetyl phenyl hydrazine

1.1 g of Phenidone (Registered Trade Mark)

25 g of Natrosol HHR 250 (hydroxyethylcellulose) (Registered Trade Mark) made up with water to 1000 ml.

20 After development for 10 minutes at 20°C the image element was separated from the cover sheet and freed from the paste adhering to it. Through the transparent support a dye image was visible on the TiO<sub>2</sub> layer as image background.

The dye giving compound was incorporated in the casting solution for the dye layer 3:

25 200 g of the dye giving compound together with 400 g of sodium salt of di(sulphonaphthyl)methane as described in Example 11 were milled in a sand mill. The obtained dispersion was divided into two parts and one part was subsequently spray dried. Then both parts are added each to 6 l of a 10% gelatine solution and after addition of a suitable wetting agent, coated to yield a dye coating of one g/m<sup>2</sup>.

30 The sensitometric assessment shows that the spray drying does not impair sensitometric properties of the photographic material. A further material was prepared for comparison with the difference that the dye was mixed with N,N-diethyl-laurinic acid amide in a ratio of one part per one part and the mixture was emulsified together with sodium dodecyl benzene sulphonate and acetic acid ester in an aqueous gelatine solution before coating the layer 3.

35 The sensitometric assessment of both samples shows that the sample in which the dye was incorporated using an auxiliary solvent had a fog higher by 0.2 density units as compared with the sample of the present invention which had a fog of 0.2 and a maximum density of 2.1.

#### WHAT WE CLAIM IS:—

40 1. A process for the incorporation of a photographic additive which is substantially insoluble in water and which is a coupler, sensitising dye, stabilizer, white toner, UV absorber or UV stabilizer into a photographic hydrophilic binder layer, in which process the additive is milled in the aqueous phase which is substantially free from organic solvents in the presence of a dispersing agent as herein defined to a particle size of less than 1 micron and the resulting aqueous dispersion is added to the hydrophilic binder casting solution.

45 2. A process as claimed in claim 1 in which the additive is incorporated into a non-light sensitive hydrophilic binder layer.

3. A process as claimed in claim 1 in which the additive is incorporated into a silver salt emulsion.

50 4. A process as claimed in claim 3 in which the additive is incorporated into a light-sensitive silver halide emulsion.

5. A process as claimed in any of claims 1 to 4 in which from 0.1 to 3 parts by weight of dispersing agent are used per 1 part by weight of photographic additive.

6. A process as claimed in any of claims 1 to 5 in which the photographic additive is a sensitizing dye or stabilizer for silver salt emulsions.

7. A process as claimed in any of claims 1 to 5 in which the photographic additive is a colour coupler, white coupler, white toner or UV-absorber.

5 8. A process as claimed in any of claims 1 to 7 in which the aqueous dispersion of the photographic additive is prepared for use by drying.

9. A process as claimed in claim 8 in which drying is carried out by freeze drying or atomisation drying.

10. A process as claimed in any of claims 1 to 9 in which the dispersing agent is a monomeric, oligomeric or polymeric alkyl-aryl sulphonate.

10 11. A process as claimed in claim 10 in which the alkyl-aryl sulphonate contains at least 18 carbon atoms.

12. A process as claimed in claim 10 in which the dispersing agent is an alkali metal salt of triisopropyl-naphthalene sulphonic acid or di-sec.-butylnaphthalene sulphonic acid.

15 13. A process as claimed in claim 10 in which the dispersing agent is a condensation product of naphthalene or ditolylether with formaldehyde and sulphuric acid or a lignin sulphonate acid.

14. A process as claimed in any of claims 1 to 13 in which the milling is carried out in a sand-mill.

20 15. A process as claimed in any of claims 1 to 14 in which the milling elements are glass beads, quartz sand or silicon carbide sand.

16. A process as claimed in any of claims 1 to 15 in which the photographic additive is a dye of any of the formulae I to XI as herein defined.

25 17. A process as claimed in any of claims 1 to 15 in which the photographic additive is a stabilizer of formula XII or XIII as herein defined.

18. A process as claimed in any of claims 1 to 17 in which the silver salt emulsion has a ratio of gelatine to silver of less than 0.7.

19. A process as claimed in claim 1 substantially as herein described with reference to the Examples.

20 20. A process as claimed in claim 1 substantially as herein described with reference to the accompanying drawings.

21. A silver salt emulsion which contains a photographic additive which has been introduced into the emulsion by a process as claimed in any of claims 1 to 20.

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COMPLETE SPECIFICATION

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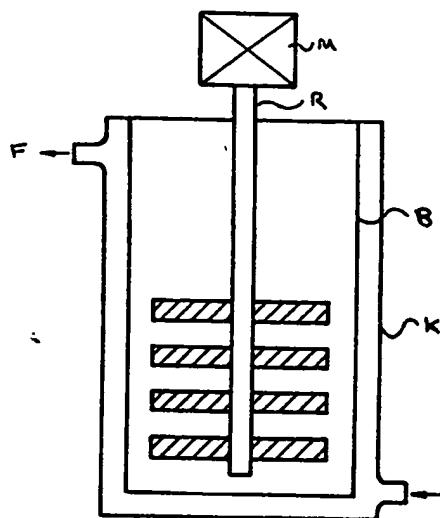


FIG. 1

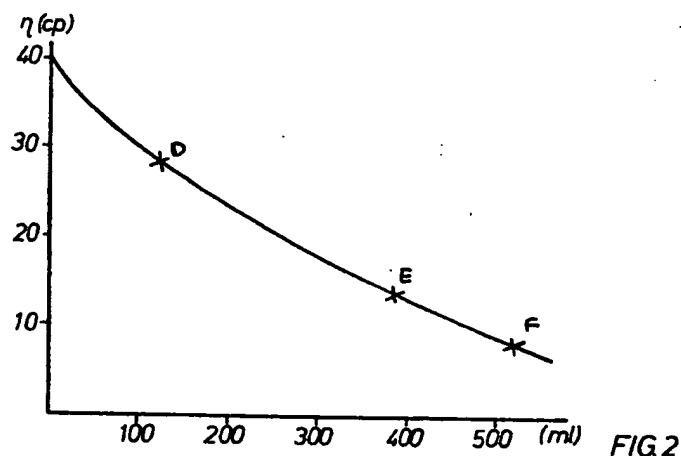


FIG. 2

1570362 COMPLETE SPECIFICATION

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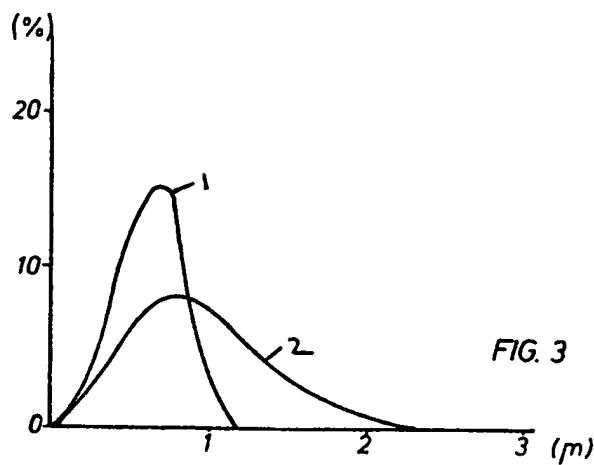


FIG. 3

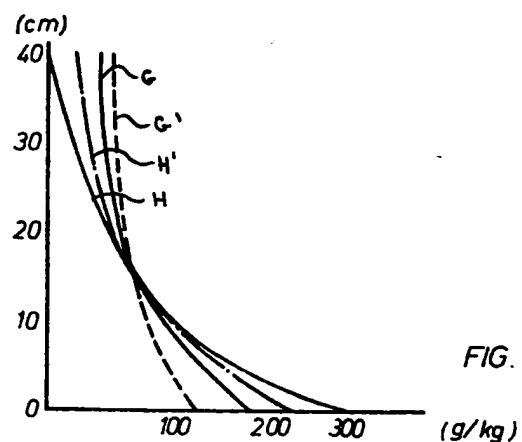


FIG. 4

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